Thermo-acoustic Study of Binary Liquid Mixture Containing Diethylenetriamine and Triethylene Glycol Using Interferometric Method with Different Frequencies and at Constant Temperature

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ABSTRACT:

The Ultrasonic velocity (U), density (ρ) and viscosity (η) of DETA with Triethylene Glycol have been measured at constant temperature 296 K and at frequencies 1MHZ, 3MHZ & 5MHZ over entire range of composition of DETA in Triethylene glycol. These acoustic parameters were used for evaluation of the acoustic parameters such as Rao's constant (R), Wada's constant (W), Vanderwaal's constant (b), classical absorption (α/f^2), fractional free volume (f), relative association (R_A), internal pressure (π_i). In addition to above parameters some excess were also evaluated. Excess internal pressure (π_i^E) and excess viscosity (η^E) have been computed and studied at constant temperature 296 K and at frequencies 1MHZ, 3MHZ & 5MHZ. This acoustical study provides very important information about the molecular interaction between the molecules of the binary liquid mixture. The molecular interactions between the components of this system have been interpreted in terms of the acoustic parameters.

KEY WORDS: Relative association, internal pressure, fractional free volume, Wada's constant, excess viscosity

INTRODUCTION:

Ultrasonic technique has become a powerful tool for physico-chemical study and molecular behavior of liquid mixtures. Ultrasonic velocity has been adequately employed in understanding the molecular interactions in liquid mixtures. Ultrasonic velocity and viscosity have been widely used in the field of structural evaluation [1]. In the present investigation the chemicals used are Diethylenetriamine and Triethylene Glycol. DETA [3] miscible in water [2] is an organic compound with formula $HN(CH_2CH_2NH_2)_2$. This is colorless hygroscopic liquid. It is soluble in water and polar organic solvents. It is not soluble in simple hydrocarbons. It is a weak base & its aqueous solution is alkaline [4]. It is common curing agent for epoxy resins in epoxy adhesives [5]. It has been evaluated for use in countermine system. It would be used to ignite and consume the explosive fill of land mines in beach and surf zones [6]. Its dielectric constant is 12.2 at 1 KHZ and polarity is approximately zero. It is non-polar. It is polydentate ligand.

Triethylene glycol or tri-glycol is a colorless odorless viscous liquid with formula HOCH2CH2OCH2CH2OCH2CH2OH. It is used as a plasticizer for vinyl polymers. It is also used in air sanitizer products such as oust [7] of clean and pure. It is an additive for hydraulic fluids and brake fluids and is also used as a base for smoke machine fluid in the entertainment industry. It is miscible with water. It is soluble in ethanol, acetone, acetic acid, glycerin, pyridine, aldehydes. It is insoluble in oil, fat and most of the hydrocarbons. It is an important non-volatile industrial solvent.

In the present study, density, viscosity and ultrasonic velocity of Diethylenetriamine with Triethylene glycol have been measured and used to compute the acoustic parameters such as Rao's constant (R), Wada's constant (W), Vanderwaal's constant (b), classical absorption (α/f^2), fractional free volume (f), relative association (R_A), internal pressure (π_i), excess internal pressure (π_i^E) and excess viscosity (η^E). These data values have been investigated at constant temperature 296 K & at frequencies 1MHZ, 3MHZ & 5MHZ. These have been used for investigations of the intermolecular interaction in this binary mixture over entire mole fraction range of DETA in Triethylene glycol.

EXPERIMENTAL:

Chemicals used are DETA and Triethylene glycol. DETA was obtained from Loba Chemicals Pvt. Ltd. Mumbai. Triethylene glycol was obtained from Qualigenes Fine Chemicals, Mumbai. Density of the pure components and their mixtures were measured by using 10 ml specific gravity bottle up to the accuracy (0.001 g) [8]. The Abbe's refractometer is very popular and owes its popularity to its convenience, its wide range (n_D = 1.3 to 1.7), and to the minimal sample is needed [9]. The accuracy of the instrument is about ±0.0002; its precision is half this figure. The improvement in accuracy is obtained by replacing the compensator with a monochromatic source and by using larger and more precise prism mounts. The former provides a much sharper critical boundary and the latter allows a more accurate determination of the prism position. The viscosity of pure liquids and their mixtures [10] were measured using Ostwald's viscometer with an accuracy of $\pm$0.001 Nsm^{-2}. Ultrasonic sound velocities were measured using multifrequency ultrasonic interferometer MX–3 (H. C. Memorial Scientific Corporation, Ambala Cantonment) with working frequencies 1MHZ, 3MHZ & 5MHZ.

From the measured values of Density (ρ), viscosity (η) and Ultrasonic velocity (U) the acoustic parameters such as Rao's constant (R), Wada's constant (W), Vanderwaal's constant (b), classical absorption (α/f^2), fractional free volume (f), relative association (R_A), internal pressure (π_i), excess internal pressure (π_i^E) and excess viscosity (η^E) have been computed and studied at constant temperature 296 K & at frequencies 1MHZ, 3MHZ & 5MHZ, in order to study the intermolecular interaction in this binary mixture over entire mole fraction range of DETA in Triethylene glycol. The standard formulae used for the computation of the above acoustical parameters are

THEORY & CALCULATIONS:

The standard equations employed for evaluation of required parameters developed by various research fellows are explained below.

1. ULTRASONIC VELOCITY: It is the velocity of the sound waves propagating through the binary liquid mixture. λ is the wavelength of the sound waves inside the binary or ternary liquid mixture.
   $U = n\,\lambda$ m/s (1)

2. RAO'S CONSTANT OR MOLAR VELOCITY: It is required in the study of acoustical properties of pure liquids & liquid mixtures. Variation in the values of Rao's constant with molar composition is an evidence of significant interaction between the components of binary or ternary system.
   $R = V_m \quad U^{1/3} \quad m^3/mole$ (2)
3. WADA'S CONSTANT: It is required in the study of acoustical properties of pure liquids & liquid mixtures. It is also known as molar compressibility. Its value depends on the structure of pure liquid or liquid mixtures. Variations in Wada's constant with mole fraction of the solute provide evidence of molecular interaction between the components of binary or ternary system.
   $W = \frac{M}{\rho}\frac{1}{\beta^{1/7}} \quad J/mol$ (3)
4. VANDERWAAL'S CONSTANT: It is required in the study of acoustical properties of pure liquids & liquid mixtures. It is also known as molar compressibility. Its value depends on the structure of pure liquid or liquid mixtures. Variations in Wada's constant with mole fraction of the solute provide evidence of molecular interaction between the components of binary or ternary system.
   $b = V_m[(1-(R_g T/M_{eff}\, U^2))(1+(M_{eff}\, U^2/\, R_g T)^{1/2})] \quad m^2/mole$ (4)
5. CLASSICAL ABSORPTION: It is also known as attenuation coefficient. It is measure of spatial rate of decrease in intensity level of the ultrasonic wave.
   $(\alpha/f^2\,) = (8\pi^2\eta)\,/\,3\rho U^3 \quad NPS^2m^{-1}$ (5)

   η is the viscosity of the binary mixture, U is the velocity of the ultrasonic wave and ρ is the density of the binary mixture

6. INTERNAL PRESSURE: It is also known as molar compressibility of the given liquid mixture. This is very large pressure. It gives idea about the solubility characteristics.
   $\pi_i = bRT \; (\frac{k\,\eta}{u})^{1/2} \, (\frac{\rho^{2/3}}{{M_{eff}}^{7/6}}) \quad Pa$ (6)

   $b = 2$, R= 8.314 J/ mol. °K, k is a constant equal to 4.28×10^9
7. FRACTIONAL FREE VOLUME: It is the ratio of available volume to molar volume of the binary liquid mixture.
   $f = \; V_a/V_m \quad m^3/mol$ (7)
8. RELATIVE ASSOCIATION: It is a parameter used to assess the association in any solution relative to association existing in water at 0 °C. it is influenced by two factors 1)the breaking up of solvent molecules on addition of electrolyte to it & 2)the salvation of ions that is simultaneously present.
   $R_A = \frac{ds}{do}\,[\frac{Uo}{Us}]^{1/3}$ (8)

   Uo & Us are ultrasonic velocities in solvent & solution respectively and ds & do respective densities.

   The values of above quoted excess acoustic parameters are computed using the general relation given below as relation 9.

9. EXCESS PARAMETERS: The general relation for evaluating various excess parameters is

$$A^E = A_{expt} - A_{id} \quad (9)$$

where A_{expt} is the experimentally determined values of any acoustical parameters and $A_{id} = \sum A_i X_i$, Ai is any acoustical parameters & X_i the mole fraction of that liquid component. The nature and degree of molecular interaction between the component molecules of the liquid mixture have been speculated through the size and extent of deviation of the excess parameters. There will be positive deviation if size of the solvent molecule is increased and if it is decreased then the deviation is negative. A stronger molecular interaction may be due to charge transfer, dipole-induced dipole and dipole-dipole interactions. It leads to more compact structure of binary or ternary liquid mixtures. Weak molecular interactions may cause expansion in the volume of the liquid mixture.

RESULTS AND DISCUSSION:

The experimentally measured values of ultrasonic velocity (U) & computed values of Rao's constant (R), internal pressure (π_i), Wada's constant (W) and Vanderwaal's constant (b) are given in table I. Other acoustical parameters classical absorption (α/f^2), fractional free volume (f), relative association (R_A), excess viscosity (η^E) and excess internal pressure (π_i^E) are listed in table II. The behavior of these parameters with increase in mole fraction of DETA and with increase in ultrasonic frequencies in the binary mixture is represented graphically in figures from 1 to 10. We have utilized these behaviors for interpretation of intermolecular interactions between the components of this liquid mixture.

The variation in the ultrasonic velocity with rise in mole fraction of DETA and with increase in ultrasonic frequencies is illustrated in figure 1. Observation of figure 1 reveals that ultrasonic velocity increases with rise in mole fraction of DETA for all the three ultrasonic frequencies. It indicates significant interaction between the components of the binary system. The variation in the internal pressure with rise in mole fraction of DETA and with increase in ultrasonic frequencies is illustrated in figure 2. Perusal of figure 2 shows that there is decrease in internal pressure with increase in concentration of DETA for all the three frequencies. It is very important parameter in the acoustical study. It is also known as molar compressibility of the liquid mixture. The decreasing trend of internal pressure with rise in concentration of DETA suggests that the strength of interaction decreases gradually with increase in concentration of the solute. In other words there is weak interaction between the unlike molecules of the binary liquid mixture [11]. The variation in the Rao's constant and Wada's constant with rise in mole fraction of DETA and with increase in ultrasonic frequencies is illustrated in figure 3 and 4 respectively. Perusal of figures 3 & 4 show continuous decrease in both Rao's constant and Wada's constant with rise in concentration of the solute DETA for all the three frequencies. This decreasing trend of Rao's & Wada's constants with rise of concentration of solute indicates that there is weak molecular interaction between component molecules of this binary liquid mixture and it is decreasing gradually with increase in solute concentration.

Table I:

The experimentally measured values of ultrasonic velocity (U) & computed values of Rao's constant (R), internal pressure (π_i), Wada's constant (W) and Vanderwaal's constant (b) are presented in table I.

Mole fraction of DETA in Triethylene glycol	U (m/s)	$\pi_i * 10^9$ (pa)	R (m^3/mol)	W (J/mol)	b (m^2/mol)
T=296°K and Frequency = 1MHZ					
0	1611.7	5.6	0.001564345	0.003003	0.000973
0.088535	1624	4.8	0.001523549	0.002915	0.000929
0.184771	1636.4	4.2	0.001485028	0.002833	0.000889
0.289757	1650	3.7	0.001448921	0.002755	0.000852
0.404743	1663	3.2	0.001414521	0.002681	0.000817
0.53123	1676	2.9	0.001381865	0.00261	0.000784
0.671035	1688.8	2.6	0.001350769	0.002543	0.000752
0.826378	1698.4	2.3	0.001320343	0.002477	0.000722
1	1706.6	2.1	0.001291003	0.002414	0.000692
T=296°K and Frequency = 3MHZ					
0	1620	5.5	0.001567025	0.003007	0.000978
0.088535	1633.56	4.8	0.001526532	0.00292	0.000935
0.184771	1646.16	4.2	0.001487975	0.002838	0.000894
0.289757	1659.6	3.6	0.001451726	0.002759	0.000857
0.404743	1672.2	3.2	0.001417125	0.002685	0.000821
0.53123	1684.8	2.9	0.00138428	0.002614	0.000788
0.671035	1696.8	2.6	0.001352899	0.002546	0.000756
0.826378	1710	2.3	0.001323343	0.002482	0.000726
1	1725	2.1	0.001295626	0.002421	0.000699
T=296°K and Frequency = 5MHZ					
0	1624	5.5	0.001568314	0.003009	0.00098
0.088535	1639	4.8	0.001528225	0.002923	0.000938
0.184771	1654	4.1	0.001490333	0.002841	0.000899
0.289757	1669	3.6	0.001454461	0.002764	0.000862
0.404743	1684	3.2	0.00142045	0.00269	0.000827
0.53123	1699	2.9	0.001388158	0.00262	0.000795
0.671035	1713.8	2.6	0.001357402	0.002553	0.000764
0.826378	1729	2.3	0.001328226	0.00249	0.000734
1	1744	2.1	0.001300366	0.002429	0.000707

Table II:

The computed values of classical absorption (α/f^2), fractional free volume (f), relative association (R_A), excess viscosity (η^E) and excess internal pressure (π_i^E) are listed in table II.

Mole fraction of DETA in Triethylene glycol	$\alpha/f^2 * 10^{-13}$ $(NPS^2 m^{-1})$	f (m^3/mol)	R_A	η^E (POISE)	$\pi_i^E * 10^8$ (pa)
T=296°K and Frequency = 1MHZ					
0	27.3766	-0.00731	1	0	0.00783626
0.088535	18.7319	-0.015	0.978581	-0.086	-2.5
0.184771	13.0918	-0.02275	0.957263	-0.12279	-3.9
0.289757	9.31188	-0.03125	0.935837	-0.12979	-4.4
0.404743	6.75267	-0.03937	0.914653	-0.11862	-4.3
0.53123	4.98028	-0.0475	0.893591	-0.09639	-3.7
0.671035	3.73252	-0.0555	0.872684	-0.06751	-2.7
0.826378	2.85461	-0.0615	0.852429	-0.03479	-1.5
1	2.21841	-0.06662	0.832483	0	-0.034196
T=296°K and Frequency = 3MHZ					
0	26.9579	-0.0125	1	0	-0.1344941
0.088535	18.405	-0.02098	0.978342	-0.086	-2.68
0.184771	12.8603	-0.02885	0.957004	-0.12279	-4.03
0.289757	9.15122	-0.03725	0.93563	-0.12979	-4.53
0.404743	6.64183	-0.04513	0.914537	-0.11862	-4.38
0.53123	4.90265	-0.053	0.893561	-0.09639	-3.76
0.671035	3.67998	-0.0605	0.872804	-0.06751	-2.78
0.826378	2.79691	-0.06875	0.851954	-0.03479	-1.55
1	2.14818	-0.07813	0.830934	0	-0.1485996
T=296°K and Frequency = 5MHZ					
0	26.7592	-0.015	1	0	-0.2E
0.088535	18.2223	-0.02438	0.978062	-0.086	-2.8
0.184771	12.6783	-0.03375	0.956275	-0.12279	-4.1
0.289757	8.99747	-0.04312	0.934638	-0.12979	-4.6
0.404743	6.50318	-0.0525	0.913146	-0.11862	-4.5
0.53123	4.78075	-0.06187	0.891798	-0.09639	-3.9
0.671035	3.57155	-0.07112	0.870624	-0.06751	-2.9
0.826378	2.70571	-0.08062	0.84952	-0.03479	-1.7
1	2.07873	-0.09	0.828586	0	-0.26

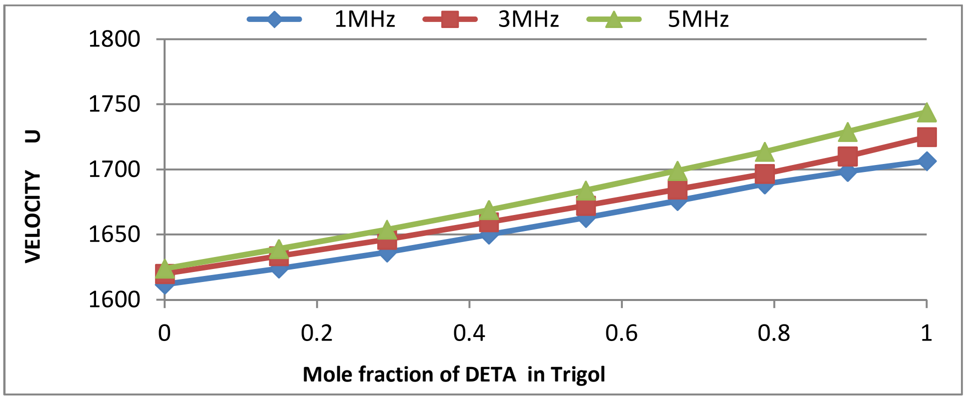

Fig 1 Graph between variation in ultrasonic velocity with rise in concentration of DETA in Triethylene glycol and with increase in ultrasonic frequencies at constant temperature

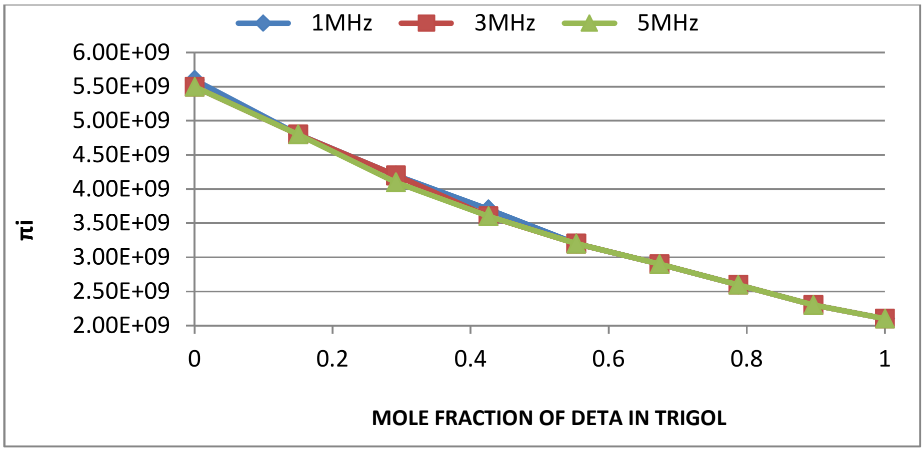

Fig 2 Graph between variation in internal pressure with rise in concentration of DETA in Triethylene glycol and with increase in ultrasonic frequencies at constant temperature

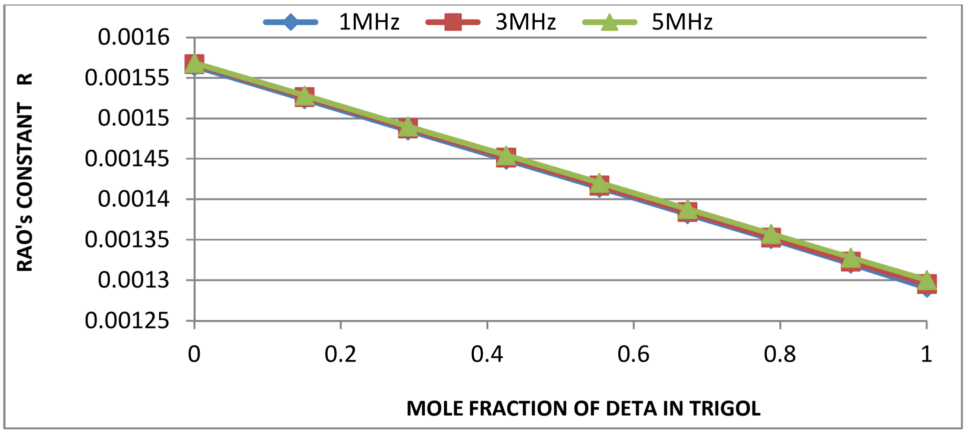

Fig 3 Graph between variations in Rao's constant with rise in concentration of DETA in Triethylene glycol and with increase in ultrasonic frequencies at constant temperature

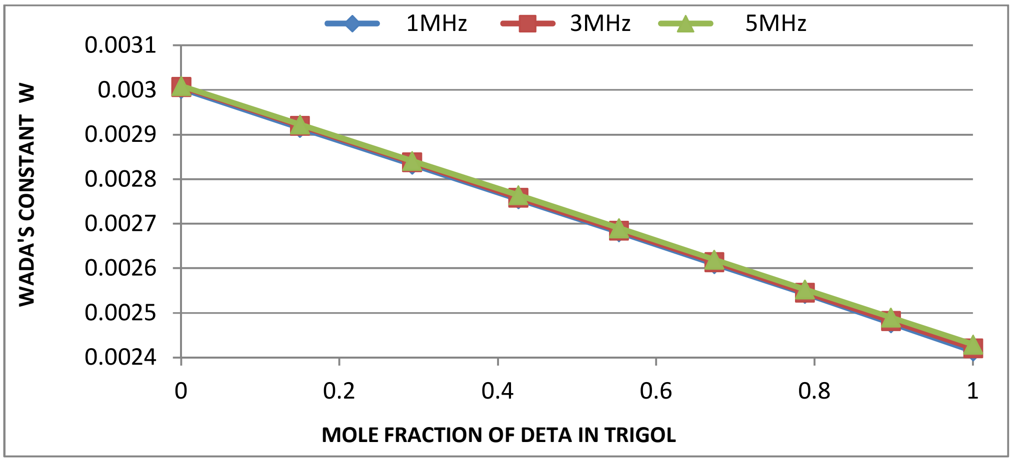

Fig 4 Graph between variations in Wada's constant with rise in concentration of DETA in Triethylene glycol and with increase in ultrasonic frequencies at constant temperature

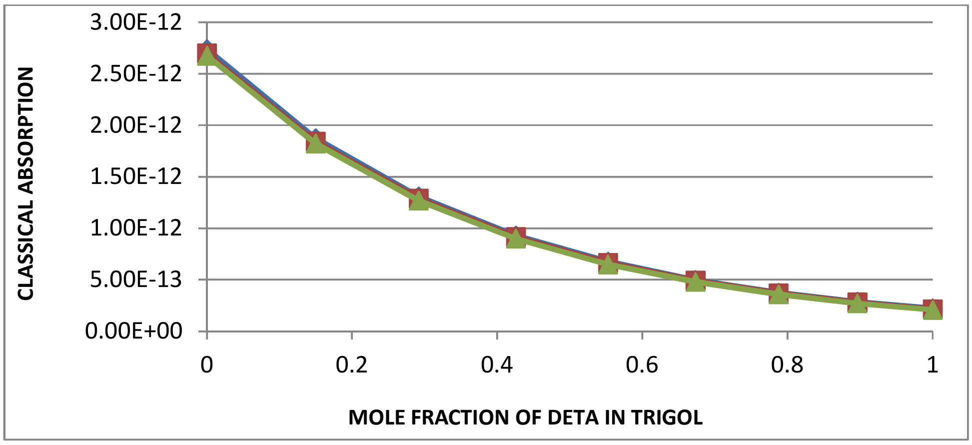

Fig 5 Graph between variations in classical absorption with rise in concentration of DETA in Triethylene glycol and with increase in ultrasonic frequencies at constant temperature

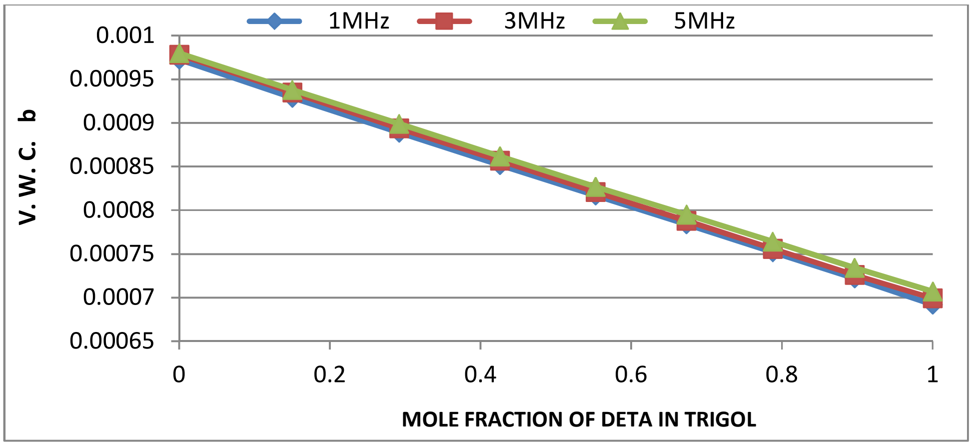

Fig 6 Graph between variations in Vanderwaal's constant with rise in concentration of DETA in Triethylene glycol and with increase in ultrasonic frequencies at constant temperature

The variation in the classical absorption and Vanderwaal's constant with rise in mole fraction of DETA and with increase in ultrasonic frequencies is illustrated in figures 5 & 6 respectively. Perusal of figure 5 shows decrease in classical absorption with increase in concentration of DETA for all the three frequencies. It indicates that there may be some sort of interaction between the molecules of the binary system. Observation of figure 6 shows that the Vanderwaal's constant decreases linearly with rise in concentration of DETA for all the three frequencies. This shows that binding forces between DETA and Triethylene glycol are becoming weaker with increase in concentration of DETA for all the three frequencies [12]. Therefore, there is existence of weak intermolecular interaction in the binary system. The variation in the fractional free volume with rise in mole fraction of DETA and with increase in ultrasonic frequencies is illustrated in figure 7. Perusal of figure 7 shows that there is decrease in fractional free volume with increase in concentration of the solute for all the three ultrasonic frequencies. It is more pronounced at higher frequencies of the ultrasonic wave. It means that enhancement of disorder is increasing with increase of ultrasonic frequencies. This absolutely supports weak intermolecular forces between the constituents of the binary mixture of DETA and Triethylene glycol.

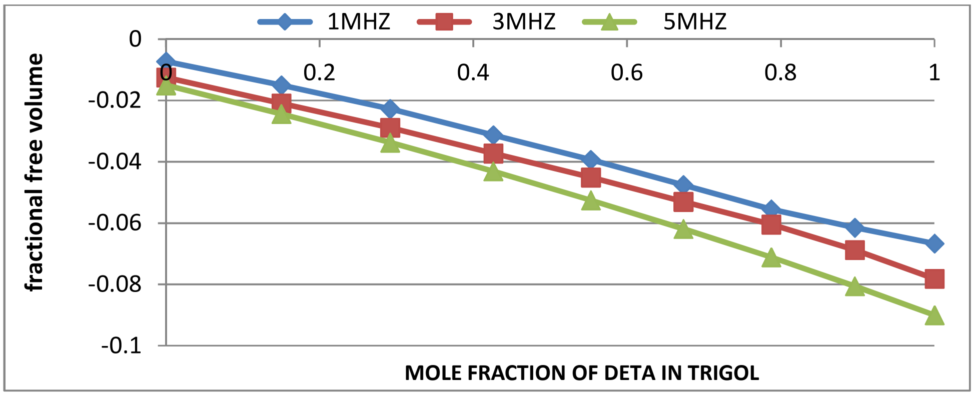

Fig 7 Graph between variations in fractional free volume with rise in concentration of DETA in Triethylene glycol and with increase in ultrasonic frequencies at constant temperature

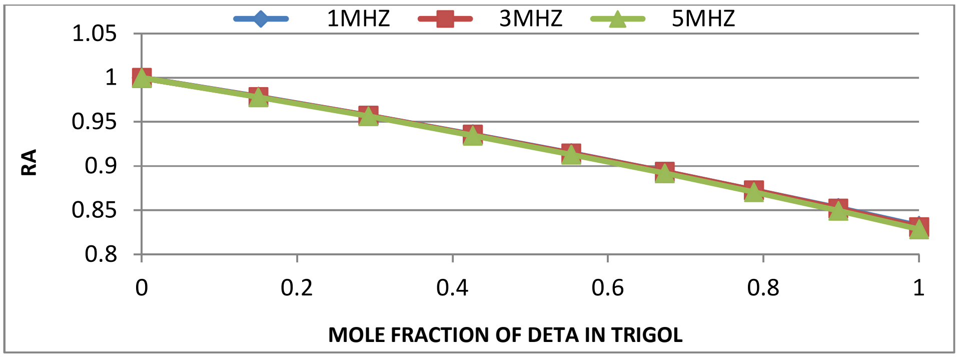

Fig 8 Graph between variations in relative association with rise in concentration of DETA in Triethylene glycol and with increase in ultrasonic frequencies at constant temperature

The variation in the relative association with rise in mole fraction of DETA and with increase in ultrasonic frequencies is illustrated in figure 8. Perusal of figure 8 shows linear and continuous decrease in relative association with increase of concentration of DETA for all the three ultrasonic frequencies. It is used to assess the association in a liquid mixture. Its decreasing trend with increase of solute and increase in ultrasonic frequencies indicates that there weak interaction between the components of the binary system [13]. Important thing to note is that the trend in figure 8 is approximately same at all the three ultrasonic frequencies.

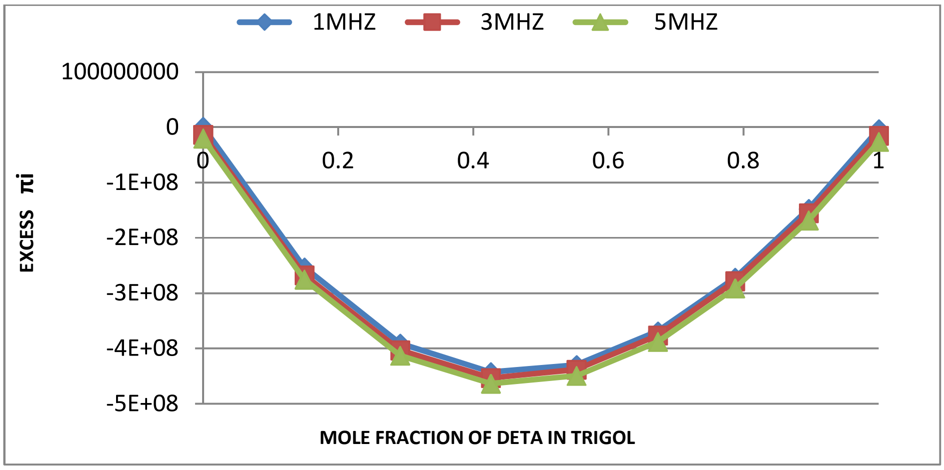

Fig 9 Graph between variations in excess internal pressure with rise in concentration of DETA in Triethylene glycol and with increase in ultrasonic frequencies at constant temperature

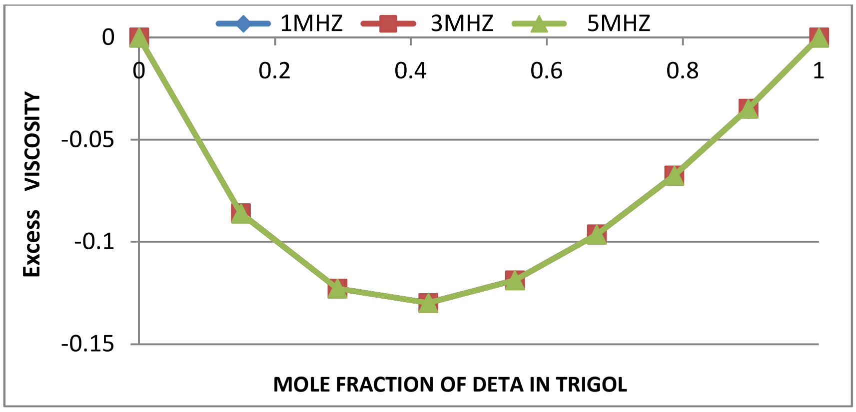

Fig 10 Graph between variations in excess viscosity with rise in concentration of DETA in Triethylene glycol and with increase in ultrasonic frequencies at constant temperature

The variation in the excess internal pressure and excess viscosity with rise in mole fraction of DETA and with increase in ultrasonic frequencies is illustrated in figures 9 & 10 respectively. Perusal of figure 9 shows negative deviation in excess internal pressure with rise of concentration of DETA for all the three frequencies. Observation of figure 10 shows negative deviation in excess viscosity with increase in concentration of DETA for all the three ultrasonic frequencies. It was reported that negative values of excess viscosity occur where weak dipole-dipole forces are primarily responsible for the weak interaction. The negative values of excess viscosity may also occur due to difference in molecular size of the component molecules of the binary system. The decreasing values of excess internal pressure reveals that the weakening of cohesive forces resulting in weaker molecular forces in the binary mixture of DETA and Triethylene glycol[14].

CONCLUSION:

In the present work various acoustical parameters are computed at constant temperature 296K and at frequencies 1MHz, 3MHz and 5MHz. The parameters Rao's constant, Wada's constant, Vanderwaal's constant, fractional free volume, relative association and few excess parameters are studied. Behaviors of almost all parameters suggest and support weak molecular interaction in this binary system. Thus, it can be concluded that there exists weak molecular interaction between the molecules the binary system consisting of DETA and Triethylene glycol at all the three ultrasonic frequencies.

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